

In situ generation of Ag nanoparticles during photopolymerization by using newly developed dyes-based three-component photoinitiating systems and the related 3D printing applications and their shape change behavior

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Abstract

Silver nanoparticles (AgNPs) play a crucial role in biology and medical research as their extensive and efficient antibacterial activity and high electrical and thermal conductivity. However, the generation of them with a certain morphology under mild conditions (under air, solvent-free, room temperature, etc.) is still a huge challenge. Herein, a simple one-step method is proposed to generate AgNPs in situ at room temperature under air by combining the photopolymerization process with the formation process of AgNPs within a few minutes. In detailed, 12 different dyes based on 2,5-diethylene-cyclopentan-1-one were first synthesized and used as high-performance type II photoinitiator. When using in conjunction of *bis*-(4-tert-butylphenyl) iodonium hexafluorophosphate (Iod) and ethyl 4-dimethylamino-benzoate (EDB), they can effectively boost the free radical photopolymerization (FRP) of polyethylene glycol diacrylate (PEG-DA) and the cationic photopolymerization (CP) of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EPOX) upon irradiation with LED@405 nm. Furthermore, all the formulations containing/without AgNPs can be successfully used to perform the direct laser write experiment. However, even if all of the obtained 3D patterns exhibited reversible swelling performance and shape-memory effects caused by swelling and dehydration for the access to 4D printing, the presence of AgNPs will affect these properties.

KEYWORDS

3D printing, nanocomposites, photopolymerization, reversible shape-memory effect, silver nanoparticles

1 | INTRODUCTION

In recent years, due to the adjustable optical properties of the metal nanoparticles (MNP) such as silver, gold or

platinum nanoparticles, the potential applications of these nano-objects in advanced materials such as photovoltaic technology,¹ electronics^{2,3} and optical detection systems,⁴ solar concentrators/reflectors or filters⁵⁻⁶ and

so forth, have attached a great attention. In order to adapt the size and the shape of the nanoparticles to these new applications, extensive researches have been made concerning the optimization of the synthesis as well as the processing of the metal nanoparticles, in order to generate nano- or micro-layers on various substrates.^{7–8} An appropriate synthetic method is the key to control the morphologies and the sizes of MNP and their subsequent physical and optical properties. Many MNP synthetic routes, for example, chemical methods, radiation methods, and solvothermal methods, and so forth, have been reported in the literature, which mainly relied on the precipitation of nanoparticles from the precursor solution upon reduction by the appropriate reducers.^{9–12} Notably, most of the procedures suffer from disadvantages. For example, several synthetic methods require sophisticated fabrication equipment, inducing expensive cost or producing particles lacking of mechanical strength, and so forth.¹³ To avoid these drawbacks, composite materials based on nanoparticles and polymer matrices have recently attracted attention due to their synergistic effects.^{14–16} Photopolymerization technology can provide a useful method to generate polymers suitable for various applications ranging from imaging, radiation curing, and optics technologies to (bio)medicine, microelectronics, and materials science, as its mild reaction conditions and controllability in time and space.^{17–19} The coordinated control of the kinetics of the two simultaneous processes of in situ photoreduction and photopolymerization can adjust the morphology of AgNPs and the properties of the nanocomposite to meet the needs of various applications. The key point of the above process is a suitable photoinitiation system, which generate highly reactive specie through a series of redox reactions under the suitable light irradiation to reduce silver cations into AgNPs. In parallel, these active substances initiate the photopolymerization of the PEG-DA to form the polymer network.^{20–22}

Although in our previous research, some monochalcone derivatives have been systematically studied as PI due to their excellent absorption properties exhibited from the UV to visible range, only some dyes ($\lambda_{\max} \geq 390$ nm) exhibited high photopolymerization efficiency for the free radical photopolymerization of acrylate upon irradiation with LED@405 nm.^{23,24} Subsequently, with aim at improving the polymerization efficiency, 10 *bis*-chalcone derivatives were also prepared, but the UV–visible spectra showed that their maximum absorption peaks basically appeared between 330 and 370 nm, which does not match to the excitation wavelength of the LED@405 nm.²⁵ Therefore, their polymerization effect is not fully optimized. So that, in this study, we hope to improve the absorption properties

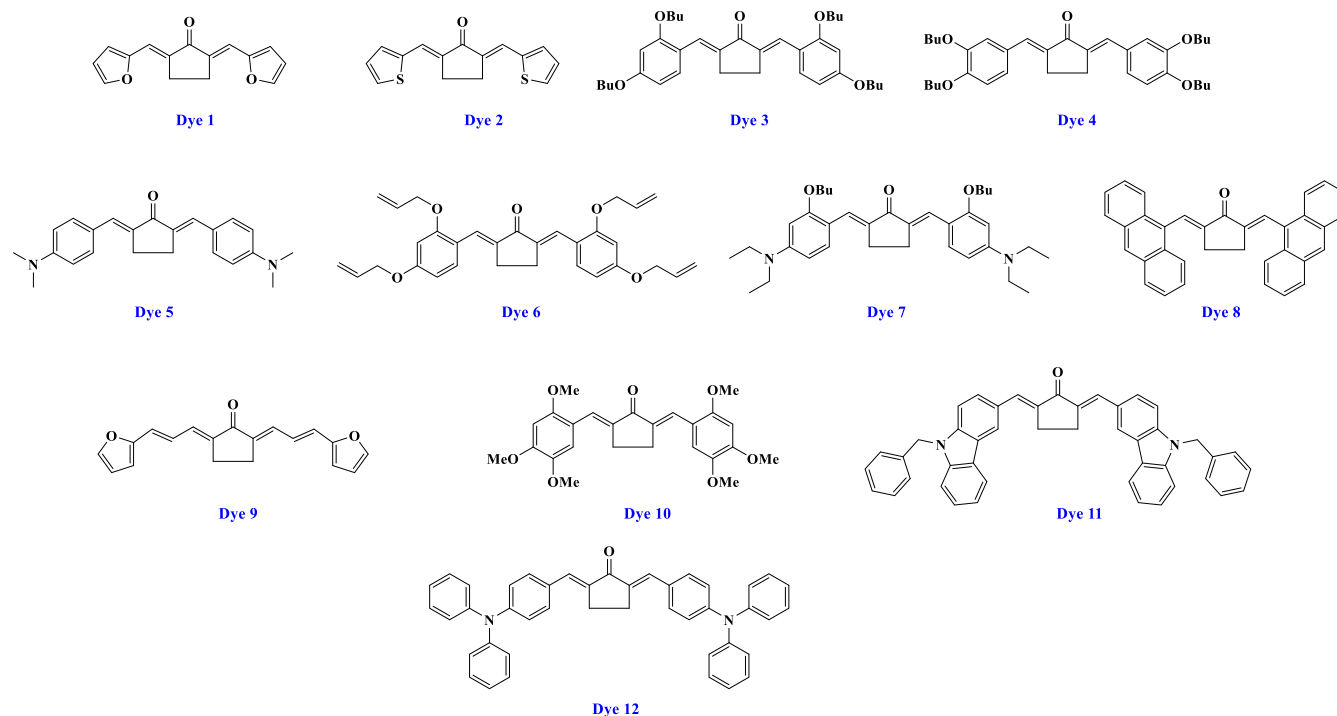
(including red-shift absorption wavelength and high molar extinction coefficient) of the *bis*-chalcone derivatives by adjusting the chemical skeleton to prepare photoinitiator that is more suitable for low-density visible light sources.

According to the abovementioned requirements, 12 novel dyes comprising the 2,5-diethylene-cyclopentan-1-one central core were first designed and synthesized. The different dyes were combined with an amine and an iodonium salt in order to form photoinitiating systems (PISs) which were evaluated for their polymerization efficiencies for the free radical polymerization (FRP) and the cationic polymerization (CP). Subsequently, the proposed photoinitiating systems were used to prepare 3D patterns with a good spatial resolution. This work proposes an efficient and environmentally friendly method combining the photopolymerization of PEG-DA and the in situ reduction of silver cations to AgNPs in order to obtain a PEG-polymer with a complete distribution of silver nanoparticles. The resulting composites not only showed reversible swelling properties but also exhibited reversible shape-memory effects. The involved chemical mechanisms during the photoreduction and photopolymerization processes were studied in detail through a series of experiments including steady-state photolysis, fluorescence quenching, electron spin resonance (ESR), and so forth. This innovative method is full of promise for the preparation of metal polymer coatings and the preparation of flexible conductive materials.

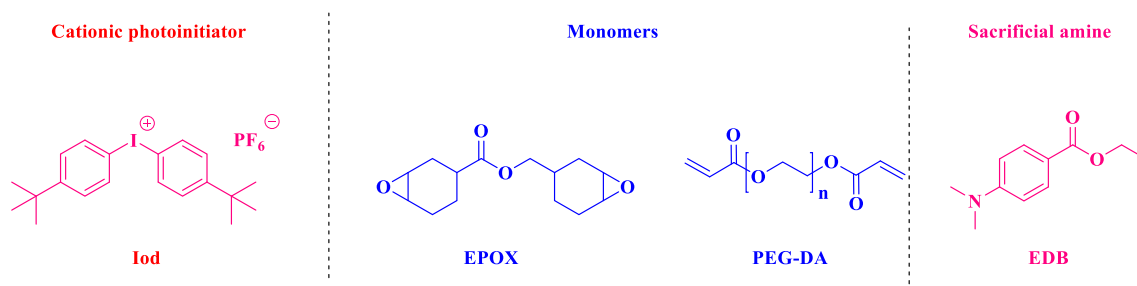
2 | MATERIALS AND METHODS

2.1 | Materials

The 12 different chalcone-based dyes (1–12) were used as photoinitiators and prepared as reported in the supporting information (S1). Their molecular structures are given in the Scheme 1. The polyethylene glycol diacrylate (PEG-DA, $M_w = 600$) was obtained from Sartomer-Europe, while the cationic photopolymerization benchmark monomer 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX) was purchased from Allnex. *Bis*-(4-*tert*-butylphenyl) iodonium hexafluorophosphate (Iod) used as the co-initiator and ethyl 4-dimethylaminobenzoate (amine, EDB) was used as the electron/hydrogen donor. The two molecules were purchased from Lambson Ltd. The radical capture agent (phenyl-*N-tert*-butylnitron - PBN) was purchased from the Sigma-Aldrich (St. Louis, MO). Their corresponding chemical structures are presented in Scheme 2. The solvents (e.g., acetonitrile, dimethyl sulfoxide and *tert*-butylbenzene) used in this study were all of analytical grade and purchased from the Sigma-Aldrich (St. Louis, MO).



SCHEME 1 Chemical structures of dyes 1–12 [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 2 Chemical structures of additives and monomers used in this study [Color figure can be viewed at wileyonlinelibrary.com]

2.2 | Free radical photopolymerization (FRP) and cationic photopolymerization (CP) initiated by dye/Iod/amine based-PIS

The dyes/Iod/amine combinations were used as PIS for FRP and CP under near UV or visible light irradiation with a LED at 405 nm ($I_0 = 110 \text{ mW/cm}^2$) and 470 nm ($I_0 = 70 \text{ mW/cm}^2$). Taking the weight of the monomer (PEG-DA or EPOX) as a reference, the content of dyes and additives is maintained at 0.1/1.5/1.5 wt%, respectively. All the dyes and additives were well-dispersed in the resins (PEG-DA and EPOX). The FRP of PEG-DA (thickness about 20 μm or 2 mm) was performed in laminated conditions to shield the radicals from being quenched by O_2 , while the CP of EPOX (thickness about

20 μm or 2 mm) was carried out in air as it is not interfered by oxygen inhibition. The conversions of epoxy or acrylate were continuously monitored by real-time FTIR spectroscopy (JASCO FTIR 4100) and followed with the representative peaks of EPOX at 790 or 3700 cm^{-1} and PEG-DA at 1600 or 6160 cm^{-1} within 200 s light irradiation.²³

2.3 | UV-visible absorption properties, photolysis, and fluorescence experiments of the dyes

UV-visible absorption properties of the 12 different chalcones and the photolysis of them based one-, two- and

three-component PIS (dyes, dyes/Iod, dyes/amine and dyes/Iod/amine) were studied using a JASCO V730 spectrophotometer. All dyes can be quickly and completely dissolved in acetonitrile, and photolysis analysis is performed at a concentration of 1×10^{-5} M, while the concentration of Iod and EDB are kept at 0.01 M. Moreover, JASCO FP-6200 fluorescence spectrophotometer was used to study the fluorescence properties of the dyes with the concentration of 1×10^{-5} M in acetonitrile.²⁶

2.4 | Redox potentials of dyes

Redox potentials (E_{ox} and E_{red}) of the different chalcones were determined by cyclic voltammetry using tetrabutylammonium hexafluorophosphate as the supporting electrolyte in acetonitrile. Free energy change ($\Delta G^{\text{S1}}_{\text{Iod}}$ or $\Delta G^{\text{S1}}_{\text{EDB}}$) for the electron transfer reaction between dyes with Iod/amine were calculated from Equations 1 or 2, where E_{ox} , E_{red} and E^* are the oxidation potential of the electron donor, the reduction potential of the electron acceptor and the excited state energy level (calculated from the crossing point of UV-visible and fluorescence spectra), respectively. According to the literature data, the reduction potential of Iod ($E^{\text{Iod}}_{\text{red}}$) was -0.7 eV and the oxidation potential of EDB ($E^{\text{EDB}}_{\text{ox}}$) was 1.0 eV.^{27–28}

$$\Delta G^{\text{S1}}_{\text{Iod}} = E_{\text{ox}} - E^{\text{Iod}}_{\text{red}} - E^* \quad (1)$$

$$\Delta G^{\text{S1}}_{\text{EDB}} = E^{\text{EDB}}_{\text{ox}} - E_{\text{red}} - E^* \quad (2)$$

2.5 | Electron spin resonance (ESR) spin trapping (ESR-ST) experiments

An X-band ESR spectrometer (Bruck EMX-plus) was used to detect the free radicals generated by the interactions between the dyes with the Iod/EDB upon LED@405 nm irradiation light which trapped by the PBN in the N_2 saturated tert-butylbenzene solution. Then simulate the detected ESR spectrum through WINSIM software.²⁹

2.6 | Preparation of silver nanoparticles (AgNPs) in DMF

Silver nanoparticles were prepared in DMF solution under air. 0.05 wt%-Dye/Iod/amine-based PIS and 4 wt %- AgNO_3 were dissolved in 10 ml DMF, after that sonicate the solution for 10 min and irradiated using a LED@405 nm ($I_0 = 110 \text{ mW/cm}^2$) to prepare the AgNPs.³⁰

2.7 | Preparation of AgNPs within PEG-polymers through in situ photopolymerization process

Dye/Iod/amine (0.1/1.51.5 wt%) and AgNO_3 (4 wt%) were dissolved in PEG-DA. The formulations were mixed with an ultrasonicator for 5 min to make the AgNO_3 well distributed before polymerization. After that, the photopolymerization profile was followed by the real-time FTIR spectroscopy and the PEG-AgNPs nanocomposite films were obtained by coating the formulation on the glass plate using Bar Coaters and curing under LED@405 nm.

2.8 | TEM experiments

After the irradiation upon LED@405 nm for 90 min, the DMF solution was ultrasonicated for 10 min and then placed on the carrier for drying to observe the morphology of the generated AgNPs. Moreover, we cut out the horizontal and vertical interfaces of the PEG-AgNPs polymers obtained after 5 min of irradiation after the RT-FTIR experiment or the composite film prepared by Bar Coaters to observe the distribution and shapes of the AgNPs generated inside. A transmission electron microscope (TEM, FEI Quanta 250 FEG) is used to detect the AgNPs in DMF solution and PEG-polymers.

2.9 | Direct laser writing (DLW) experiments

Direct Laser Writing (DLW) experiments were carried out using a computer programmed laser diode at 405 nm (Thorlabs, spot size is about $50 \mu\text{m}$). Photosensitive formulations containing PEG-DA, dyes-based PIS with/without AgNO_3 under solvent-free conditions were photopolymerized under air and the obtained 3D patterns were analyzed using a numerical optical microscope (DSX-HRSU from Olympus Corporation).³¹

2.10 | Water swelling performance of PEG-polymers and composites containing/without AgNPs

The swelling properties of PEG-polymers containing/without AgNPs were investigated by immersion in deionized water at ambient temperature. The polymers ($n = 3$) were then taken out to measure the wet weight (W_t) and the volume (V_t) after reaching the swelling

equilibrium and compared with their initial wet weight (W_0) and the initial volume (V_0). Thereafter, the swollen polymers were put in a 50°C oven to remove the absorbed water. The swelling ratio of weight (S_r) and volume (R) were defined by Equations 3 and 4, respectively.^{24,32}

$$S_r (\text{wt}\%) = (W_t - W_0) / W_0 \times 100 \quad (3)$$

$$R (\text{wt}\%) = (V_t / V_0) \times 100 \quad (4)$$

2.11 | Shape-memory effect of PEG-polymers containing/without AgNPs (4D behavior)

The shape memory effect of the PEG-polymers containing/without AgNPs is driven by water swelling and heat dehydration, specifically through the following steps: the first step is to immerse the polymers in deionized water for 1 min; the second step is to taken out the deformed polymers and placed in an oven at 80°C to dehydrate for 10 min; and the third step is to remove the deformed polymers into room temperature to restore its original shape.

3 | RESULTS AND DISCUSSION

Photophysical properties as well as the chemical mechanisms involved while using the 12 different dyes as photoinitiators were investigated in detail. Markedly, five of the new proposed dyes were never synthesized prior this work (i.e., Dyes 3, 4, 6, 7, and 11).

3.1 | UV-visible absorption properties of the different chalcones in acetonitrile

It can be seen from Figure S1 that all dyes exhibited a strong absorption peak in the visible light region ($\lambda > 390$ nm) as dissolved in acetonitrile. In addition, a weaker absorption or shoulder can also be observed in the ultraviolet range ($\lambda < 300$ nm) for dyes 3, 5, 7, 8, 9, 10, 11, and 12. Interestingly, absorption maxima ranging between 460 nm and 480 nm were detected for dyes 5, 7, and 12 exhibiting the most red-shifted absorptions. Conversely, absorption maxima lower than 460 nm were found for the other dyes. In the view of the fact that absorption maxima ranging between 460 and 480 nm were detected for dyes 5, 7, and 12 exhibiting the most red-shifted absorptions, while absorption maxima lower than 460 nm were found for the

other dyes, LED @ 405 and 470 nm were using as light irradiation sources for this work in order to ensure a good overlap between the emission spectrum of the light source and the absorption spectra of the dyes. Except for dye 8 for which a molar extinction coefficient that lower than $5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ was determined, the other dyes exhibited high molar extinction coefficients (ϵ_{max}) in the visible range that summarized in Table 1 (e.g., 58,500, 13,620, and $52,680 \text{ M}^{-1} \text{ cm}^{-1}$ for dye 7 at λ_{max} , $\lambda_{@405\text{nm}}$ and $\lambda_{@470\text{nm}}$, respectively) corresponding to π - π^* electronic transitions. In addition, the different substituents attached to the central part of 2,5-dimethylenecyclopentan-1-one strongly affected their UV-visible absorption spectra. Remarkably, the introduction of electron-donating groups caused a red-shift of the absorption spectra. Therefore, the electron donating ability of the peripheral groups can be arranged using the following order: dye 7 > dyes 5 and 12 > dyes 9 and 10 > dyes 11 and 8 > dyes 3, 4 and 6 > dyes 1 and 2.

3.2 | Photopolymerization kinetics

3.2.1 | Free radical polymerization kinetics of PEG-DA

Photoinitiation abilities of the different dye/Iod/amine (0.1/1.5/1.5 wt%) based three-component PISs for the FRP of PEG-DA were studied under a LED@405 nm or 470 nm at ambient temperature. The different polymerization profiles can be found in Figure 1, and the final acrylate function conversions (FCs) are given in Table 2. It can be seen that all the dyes-based PISs exhibited better photoinitiating efficiencies than the blank PIS (FC = 76%) simply consisting of the co-initiators (Iod/amine, 1.5/1.5 wt%) upon irradiation with the LED@405 nm at the thickness about 20 μm (See Figure 1 (A) with much better polymerization rate in presence of dyes). It demonstrated that the presence of the dyes was crucial to boost their polymerization performances. Remarkably, dyes 2, 3, 8 and 9-based PISs achieved more than 90 wt% of double bond conversions for the monomer within 50 s, which were much higher and faster than that obtained with the other dyes-based PISs.

Under the same conditions, for thick samples for which the thickness was about 2 mm, surprisingly, only dye 5-based PIS showed better photopolymerization kinetics in comparison to the blank PIS (conversion: 92% of dye 5 vs. 87% for the blank), while the conversions obtained with the other dyes-based PIS were lower than 70%, even after 200 s of irradiation. It can be ascribed to the fact that the darker color of the photopolymerizable resin and the faster surface polymerization speed, which inhibits the penetration of light and leads to an internal

TABLE 1 Light absorption properties of dyes 1–12 in acetonitrile: Maximum absorption wavelengths $\lambda_{\max}$; extinction coefficients at $\lambda_{\max}$ ($\epsilon_{\max}$) and the emission wavelength of the LED@405 nm ($\epsilon_{@405\text{nm}}$) and 470 nm ($\epsilon_{@470\text{nm}}$)

Chalcone-based dyes	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($\text{M}^{-1} \text{cm}^{-1}$)	$\epsilon_{@405\text{nm}}$ ($\text{M}^{-1} \text{cm}^{-1}$)	$\epsilon_{@470\text{nm}}$ ($\text{M}^{-1} \text{cm}^{-1}$)
1	396	41,980	37,050	270
2	392	40,840	33,590	110
3	400	41,770	41,610	2720
	274	69,250		
4	399	42,500	41,580	1280
5	460	57,400	23,700	53,446
	274	37,300		
6	397	38,150	36,700	1710
7	485	65,670	16,200	59,370
	278	22,680		
8	418	6970	6800	1600
	268	12,890		
9	428	61,130	50,310	16,540
	283	15,340		
10	427	42,062	32,270	14,380
	280	14,160		
11	421	36,350	30,560	10,160
	236	46,810		
12	460	47,620	25,300	44,400
	298	35,060		

light filtering effect. Photoinitiation ability for the EDB/Iod blank is ascribed to the formation of a light active charge transfer complex only absorbing in the near UV range.³³

More interestingly, upon irradiation with the LED@470 nm, the blank control based on the Iod/amine PIS could not lead to the photocuring of both samples with the thicknesses of 20 μm and 2 mm, while better photopolymerization kinetics could be observed for all the dyes-based PISs. Furthermore, as shown in Figure 1 (C), for thin samples, the double bond conversions achieved with the different dyes-based PISs were lower than 90% under the irradiation of the LED@470 nm, which was lower than that achieved upon irradiation of the LED@405 nm. Conversely, for thick samples, the dye 5-based PIS could achieve the best effectiveness (see Figure 1(D)) which can be assigned to its high molar extinction coefficients at the different wavelengths used for photoinitiation (e.g., 63,170, 27,360, and 58,880 $\text{M}^{-1} \text{cm}^{-1}$ for dye 5 at $\lambda_{\max}$, $\lambda_{@405\text{nm}}$ and $\lambda_{@470\text{nm}}$ respectively, see Table 1).

In comparison with the initiation ability including the final double bond conversions of the monomer (See Table 2) and the rates of polymerization (the initial slope of the curves, Figure 1) obtained for all dyes-based PISs, the LED@405 nm is proved to be a more appropriate

light source to initiate the FRP of PEG-DA than the LED@470 nm. Under these conditions, dyes 2, 3, 5, 8, and 9 were selected as the excellent candidates to boost the polymerization of PEG-DA for samples with thicknesses of 20 μm or 2 mm in laminate, perfectly matching with their high molar extinction coefficients at 405 nm.

3.2.2 | Cationic polymerization kinetics of EPOX

Photoinitiation abilities of the proposed dyes-based PISs for the CP of the EPOX were also studied upon irradiation with the LED @405 nm under air. As shown in Figure 2, the photopolymerization rate (the initial slope of the curves) of all photosensitive formulations containing dyes-based PISs were much faster than that of the blank PIS (Iod/EDB without dye), while only the final conversion achieved with the dye 6-based PIS could outperform that obtained with the blank PIS (92% of dye 6 vs. 77% of blank, as given in Table S1), confirming the crucial effect of the three-component PIS for the overall photopolymerization performance. In addition, thick samples could not be cured in depth, while thin samples could be efficiently polymerized under the same conditions suggesting the presence of an inner filter effect.

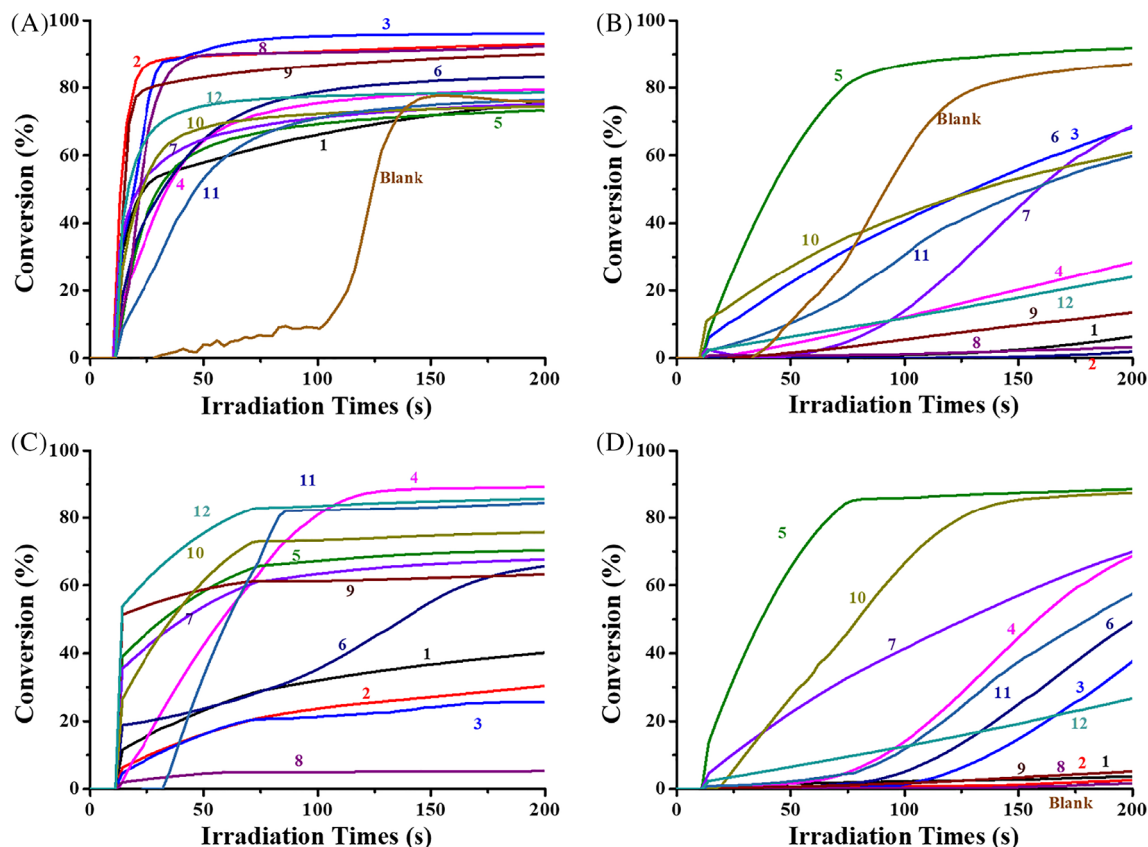


FIGURE 1 Photopolymerization profiles of PEG-DA (conversion of C=C bonds vs. irradiation time) initiated by dyes/Iod/amine (0.1/1.5/1.5 wt%) in laminate with different conditions, (A) irradiation by LED@405 nm ($I_0 = 110 \text{ mW/cm}^2$) with the thickness about $20 \mu\text{m}$; (B) irradiation by LED@405 nm ($I_0 = 110 \text{ mW/cm}^2$) with the thickness about 2 mm ; (C) irradiation by LED@470 nm ($I_0 = 70 \text{ mW/cm}^2$) with the thickness about $20 \mu\text{m}$; (D) irradiation by LED@470 nm ($I_0 = 70 \text{ mW/cm}^2$) with the thickness about 2 mm , the irradiation starts from $t = 10 \text{ s}$ [Color figure can be viewed at wileyonlinelibrary.com]

Efficiency of the PIS is clearly governed by the photochemical reactivity of the dyes with Iod and amine as well as the facility to generate cations ($\text{dye}^{\bullet+}$) (as shown in the chemical mechanisms depicted below).

3.2.3 | Free radical polymerization initiated by dyes 3 and 5-based two-component PISs or only dyes as the PIs

The laser write experiments were mainly performed using dyes 3 and 5-based formulations (see below). Therefore, the photoinitiation ability of the two-component PIS of (a) dye 3 or 5/Iod (0.1/1.5 wt%) and dye 3 or 5/EDB (0.1/1.5 wt%) and (b) dye 3 or 5 alone used as PI (0.1 wt%) for PEG-DA were studied to emphasize the important effect of the dye/Iod/amine based three-component PIS on the overall performances. As depicted in the Figure 3 and Table S2, deep curing cannot

be observed either for thin samples or thick samples for formulations containing dyes 3 or 5 as PIs. Upon the addition of Iod, thick samples could also not be cured in depth, while thin samples could be polymerized. However, the final double bond conversions of the monomer were slightly lower than that achieved with the dyes 3 or 5/Iod/amine-based PISs (e.g. FCs $\sim 90\%$ of dye3/Iod vs. $\sim 96\%$ of dye3/Iod/amine). Furthermore, with the addition of amine, the initiation ability of the dye 3/amine combination for the thin sample was much lower than that achieved with the dye 3/Iod/amine-based three-component PIS (FC $\sim 63\%$ for dye3/amine vs. $\sim 96\%$ for the dye3/Iod/amine system). Besides, thick samples could not be deeply cured with the dye 3/EDB two-component system. For the dye 5/EDB PIS, polymerization efficiencies determined for thin samples and thick samples were slightly lower than that obtained with the three-component dye 5/Iod/EDB-based PIS under the same conditions. The above results proved that the

TABLE 2 The FCs for the PEG-DA monomer initiated by dye/Iod/amine-based PISs with the thickness about 20 μm or 2 mm under LED@405 nm or LED@470 nm. The blank corresponds to the Iod/amine PIS without dyes

Final double bond conversions (FC) initiated by dye/Iod/amine-based PIS				
Dyes	LED@405 nm		LED@470 nm	
	Thickness $\sim 20 \mu\text{m}$	Thickness $\sim 2 \text{ mm}$	Thickness $\sim 20 \mu\text{m}$	Thickness $\sim 2 \text{ mm}$
1	76%	7%	40%	—
2	93%	—	30%	—
3	96%	69%	25%	39%
	80%	29%	89%	69%
5	73%	92%	70%	89%
6	83%	—	66%	50%
7	75%	69%	68%	70%
8	92%	—	5%	—
9	90%	14%	63%	—
10	75%	61%	76%	88%
11	76%	60%	85%	58%
12	79%	24%	86%	27
Blank	76%	87%	—	—

Note: “—” means not deep curing after irradiation for 200 s.

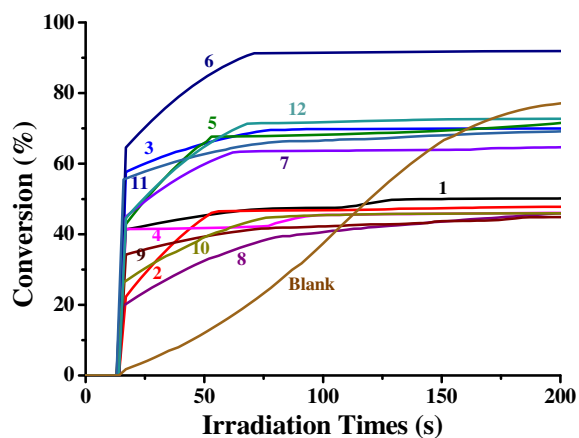


FIGURE 2 Cationic polymerization profiles of EPOX (conversion of epoxy functions vs. irradiation time) initiated by dyes/Iod/amine (0.1/1.5/1.5 wt%, wt/wt/wt)-based PIS in air under LED@405 nm ($I_0 = 110 \text{ mW/cm}^2$) with a thickness of 20 μm . The irradiation starts at $t = 10 \text{ s}$ [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

coexistence of dyes, Iod and amine had a huge effect on improving the efficiency of FRP for PEG-DA.

3.3 | Proposed chemical mechanisms

With their high reactivity, dyes 3 and 5 were chosen as representative derivatives to study the chemical mechanisms.

3.3.1 | Steady state photolysis

Steady-state photolysis experiments of the dyes, dyes/Iod, dyes/amine as well as the dyes/Iod/amine combination were carried out in acetonitrile upon irradiation with a LED@405 nm. As evidenced by the UV-visible absorption spectra in Figure 4, obvious photolysis and significant declines of the absorption intensity were observed within 2 min. In the case of dye 3-based PIS, three changes can be observed for dye 3 alone during the photolysis process, but only the main absorption peak near 400 nm decreased upon irradiation, and 15% consumption of dye 3 could be determined, which was closed to that achieved with the dye 3/EDB PIS for which only a decrease of the absorption peak at 400 nm could be observed. Furthermore, two changes can be detected for the dye 3/Iod-based PIS, which achieved 35% consumption for dye 3. The main absorption peak near 400 nm decreased while the absorption peak around 350 nm increased with the light irradiation. The dye/Iod/amine-based PIS achieved the highest consumption of dyes ($\sim 42\%$) within 120 s and the main absorption peak near 400 nm also decreased.

Remarkably, the photolysis process of the dye 5-based one/two or three-component PISs were different from that determined for the dye 3-based PISs, as shown in Figure 5. Consumptions of dye 5 in the different experiments are given in Table S2. The dye 5/Iod- and dye

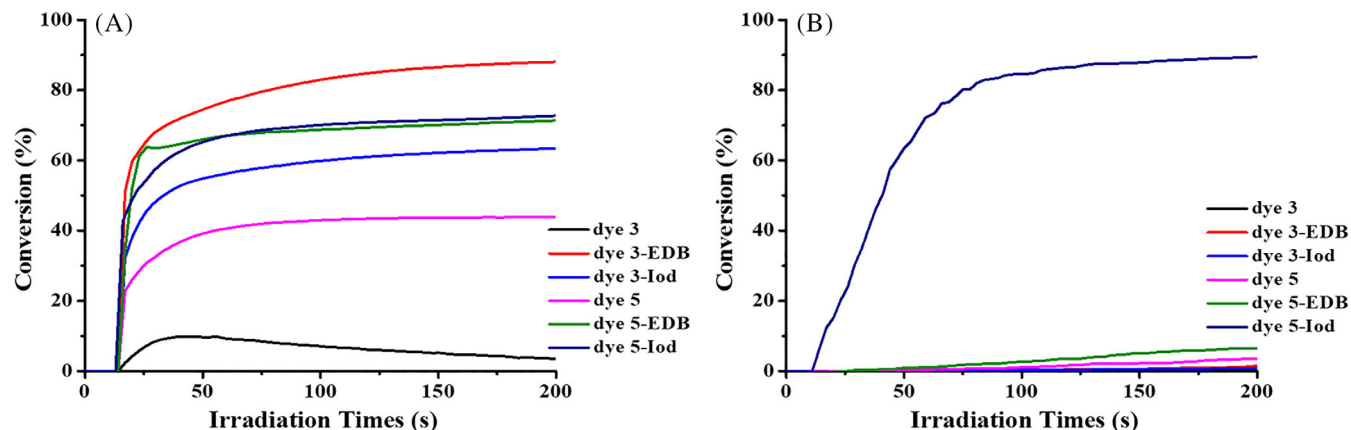


FIGURE 3 FRP profiles of PEG-DA (conversion of C=C bonds vs. irradiation time) under LED@405 nm ($I_0 = 110 \text{ mW/cm}^2$) with the thickness (a) about 20 μm and (B) about 2 mm, initiated by 0.1 wt% dye 3, 0.1 wt% dye 3/1.5 wt% Iod, 0.1 wt% dye 3/1.5 wt% EDB, 0.1 wt% dye 5, 0.1 wt% dye 5/1.5 wt% Iod and 0.1 wt% dye 5/1.5 wt% EDB. The irradiation starts from $t = 10 \text{ s}$ [Color figure can be viewed at wileyonlinelibrary.com]

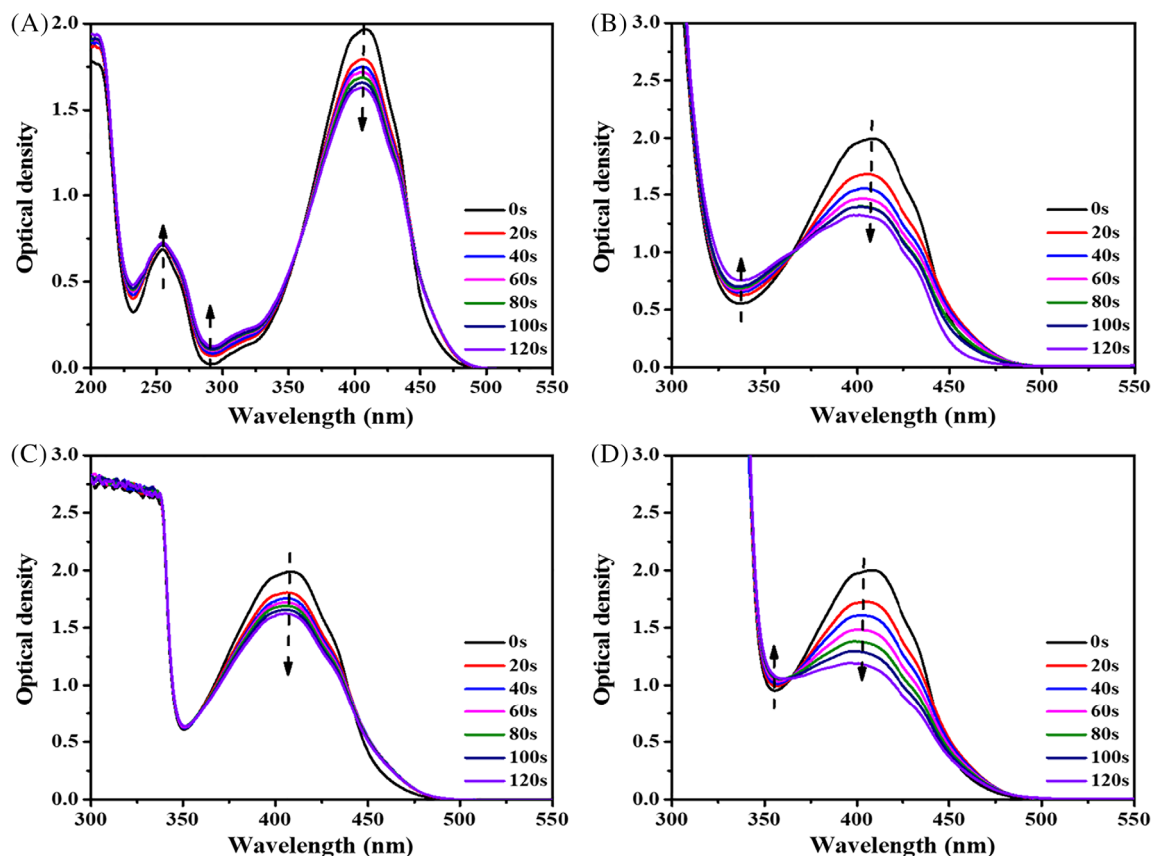


FIGURE 4 Photolysis of (A) dye 3; (B) dye 3/Iod; (C) dye 3/amine and (D) dye 3/Iod/amine upon exposure to a LED@405 nm under air in acetonitrile [Color figure can be viewed at wileyonlinelibrary.com]

5/Iod/amine-based PIS exhibited a rapid photolysis so that the main absorption peak near 450 nm showed a blue-shift and disappeared within 25 s. Consumption of dye 5 reached approximately 80% with these two systems (Figure S2). However, no obvious photolysis could be

detected with the dye 5- and dye 5/amine-based PISs, which just realized 5% consumption of dyes after 25 s. Since the rate of the photolysis process depends on the ability of the dye to transfer an electron with Iod or the amine, the above photolysis results clearly evidenced that

dye 5 can initiate faster electron transfer with Iod and amine than dye 3. This difference of reactivity can be confidently assigned to the presence of the additional amino group contained in the chemical structure of dye 5.

3.3.2 | Fluorescence quenching experiments

Emission and fluorescence quenching spectra of dyes 3 and 5 were recorded in acetonitrile and the different curves are presented in Figure S3. The addition of Iod or amine to dyes 3 or 5 resulted in a decrease of the emission intensity of dyes 3 and 5, demonstrating that Iod and EDB can act as efficient quenchers by interaction of the dye with Iod or amine in the singlet excited state. It is noticeable that the fluorescence quenching process caused by the interaction of the dye with Iod is basically linear. In addition, the Stern-Volmer coefficient (K_{SV} , Table 3) and the electron transfer quantum yield (Φ_{et} , Table 3) related to the electron transfer reaction between the dye with Iod or amine can be determined by Equation 5.^{34,35}

$$\Phi_{et} = K_{sv}^*[\text{Iod or amine}]/(1 + K_{sv}^*[\text{Iod or amine}]) \quad (5)$$

The theoretical feasibility of the interactions between dye/Iod (or dye/amine) was also investigated by calculating the free energy changes of the electron transfer reactions (ΔG_{Iod} or ΔG_{EDB} , respectively). The first singlet excited state energy (E_{S1}) is calculated from the crossing point between the standardized absorption and fluorescence spectra (e.g., $E_{S1} = 2.74$ and 2.50 eV for dye 3 and dye 5, respectively; See Table 3). Figure 6 showed the oxidation and reduction potentials of dyes 3 and 5 measured by cyclic voltammetry. It is obviously that two oxidation peaks are observed in the positive potential range of dye 5, which corresponds to irreversible further oxidation even at higher potentials. Reduction peaks could be also clearly observed. For dye 3, an oxidation peak and a reduction peak could be detected by cyclic voltammetry. According to the Equations (1) or (2), ΔG_{Iod} or ΔG_{EDB} were determined from the oxidation potential E_{ox} (or from the reduction potential E_{red}), and the first singlet excited state energy (E_{S1}) that all of them were all less than 0 except the ΔG_{EDB} of dye 5 was 0. All these results revealed that the electron transfer reactions can be occurred between dyes/Iod and dyes/amine.

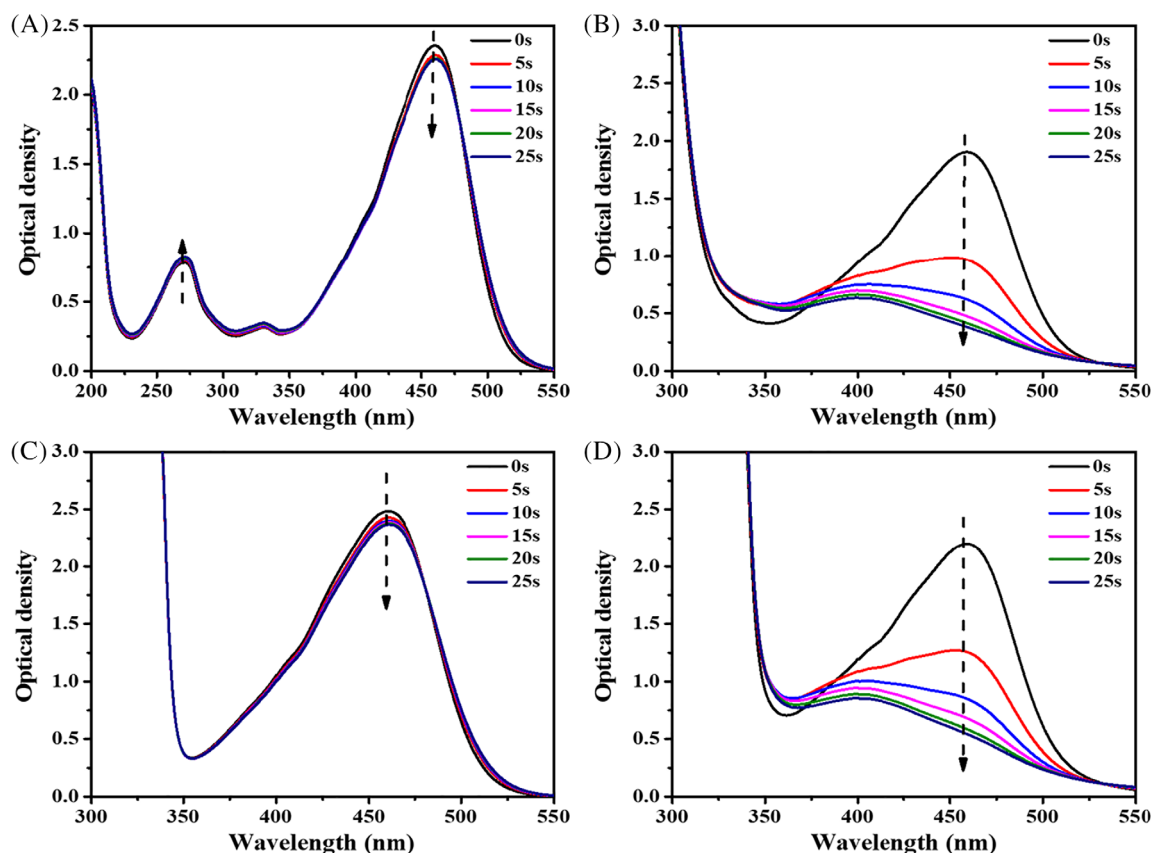


FIGURE 5 Photolysis of (a) dye 5; (B) dye 5/Iod; (C) dye 5/amine; and (D) dye 5/Iod/amine upon exposure to a LED@405 nm under air in acetonitrile [Color figure can be viewed at wileyonlinelibrary.com]

3.3.3 | ESR experiments

ESR-spin trapping experiments were successfully performed under N_2 to detect the generated radicals from the dye 5/Iod and dye 5/amine solutions. As shown in the Figure S4(A,B), aryl radicals generated by the dye 5/Iod combination could be trapped with PBN so that hyperfine coupling constants for nitrogen and hydrogen of $a_N = 14.4$ G and $a_H = 2.2$ G could be determined.

TABLE 3 Parameters characterizing the fluorescence properties of dyes 3 and 5 in acetonitrile, redox potential (E_{ox}/E_{red}) as well as the free energy change of the singlet electrode (ΔG_{S1})

	Dye 3	Dye 5
$K_{sv}^{Iod} (M^{-1})$	93	58
Φ_{et}^{Iod}	0.74	0.65
$K_{sv}^{Amine} (M^{-1})$	11	10
Φ_{et}^{Amine}	0.49	0.44
$E_{S1}(eV)$	2.74	2.50
$E^{ox}(eV)$	1.33	0.79
$E^{red}(eV)$	−1.60	−1.50
ΔG_{S1}^{Iod}	−0.71	−1.01
ΔG_{S1}^{EDB}	−0.14	0

These values were completely consistent with the literature³⁶ and also proved the occurrence of an interaction between dye and Iod as shown in the Scheme 3. Furthermore, the $a_N = 14.4$ G and $a_H = 2.2$ G detected from the dye 5/amine solution (Figure S4(C,D)) evidenced the generation of aminoalkyl radicals according to experimental data published elsewhere ($a_N = 14.4$ G and $a_H = 2.2$ G,³⁷).

3.4 | The generations of AgNPs in DMF solution and PEG-polymers

In this study, we proposed that through redox reactions between dyes and the additive (Iod/amine) a series of free radicals and cations could be generated upon irradiation with a LED@405 nm (as shown in Scheme 3), which demonstrated two roles: one was to induce the polymerization of PEG-DA monomers, and the other was to reduce the $AgNO_3$ into AgNPs in situ. The formation of AgNPs in DMF can be clearly evidenced by UV-visible absorption spectroscopy, which can also be demonstrated by the color change of the solutions. As shown in Figure 7(A), two absorption peaks at 400 nm and 460 nm can be observed, with a decrease of the absorption peak at 460 nm during photolysis of dye 5, while the intensity

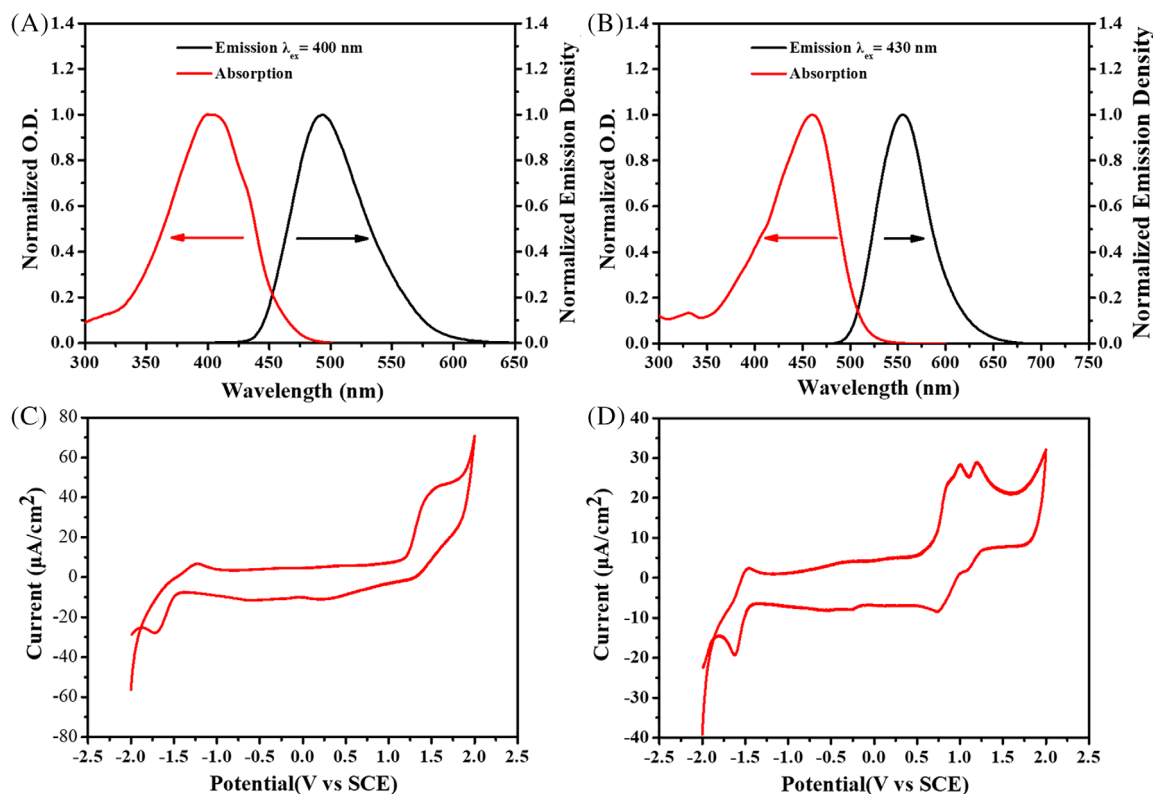
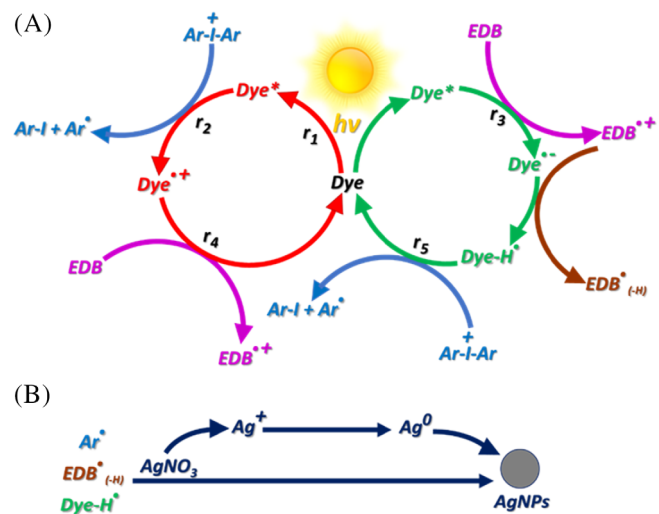


FIGURE 6 Singlet state energy of (A) dye 3; (B) dye 5 determined in acetonitrile and the cyclic voltammograms of (C) dye 3 and (D) dye 5 in acetonitrile against saturated calomel electrode (SCE) for N_2 saturated solutions [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 3 (A) Proposed photoinitiation step mechanisms of dyes/Iod/amine initiating systems; (B) Photoinitiation mechanism of the generation of AgNPs [Color figure can be viewed at [wileyonlinelibrary.com](#)]

of the absorption peak at 400 nm increased due to the generation of AgNPs upon irradiation for 90 min. Additionally, color of the solution changed from light brown to dark brown. Even, one side of the cuvette wall adopted a silver color, resulting from the coating by silver nanoparticles (see in Figure 7(B)).

Furthermore, the AgNPs generated in PEG-polymers were characterized through the changes of the color of the PEG-monomer polymerized upon irradiation with LED@405 nm (see in Figure 7(D)), which was monitored by RT-FTIR. The color also changed from light brown to dark brown, while the same changes can also be observed when coating thin films from 4 passes to 20 passes (the thickness of one pass is about 50 μm). However, although the polymerization efficiency of the formulation containing AgNPs shown in Figure 7(C) is lower than that obtained for the formulation without AgNPs, its final acrylate function conversion was still about 80% after irradiation for 300 s.

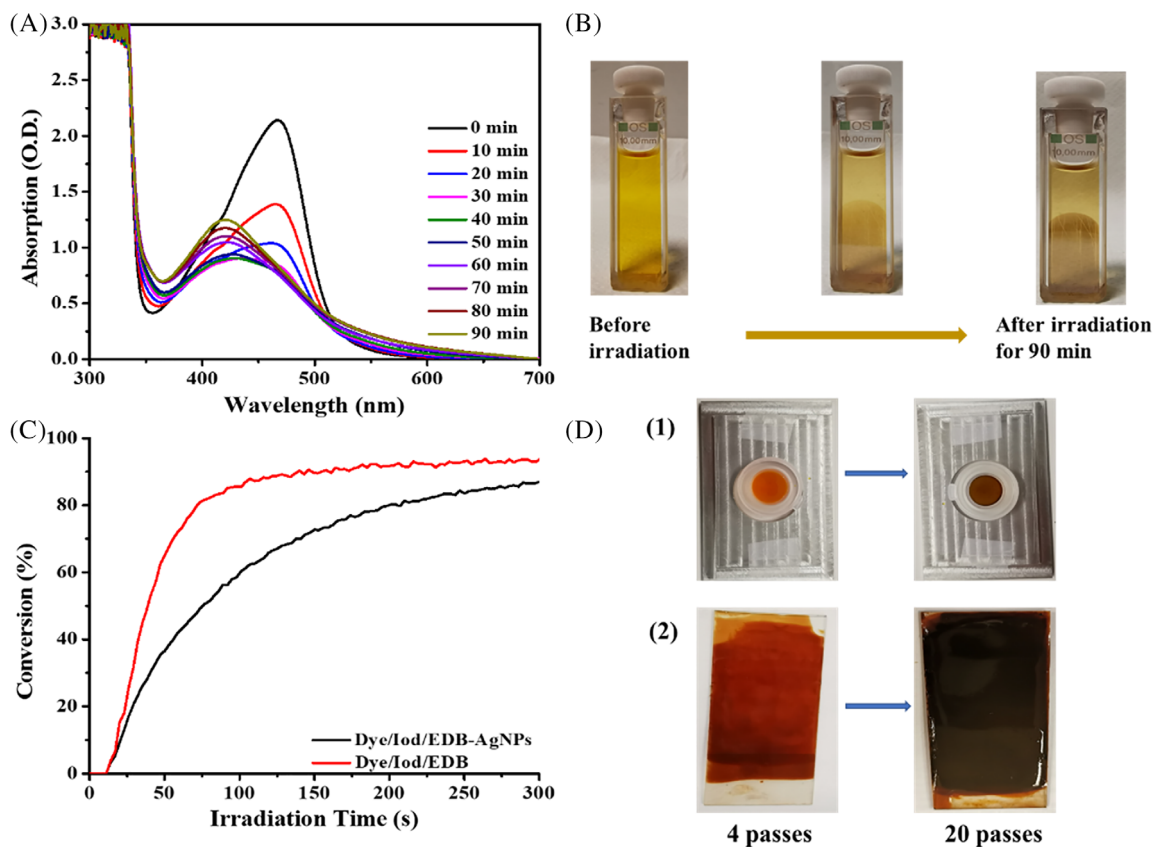


FIGURE 7 (A) In situ preparation of AgNPs with dye 5/Iod/EDB (0.05 wt%) and AgNO_3 (4 wt%) in DMF followed by UV-visible absorption spectroscopy in air atmosphere; (B) the color of solution turned to dark brown after 90 min light irradiation; (C) photopolymerization profiles of PEG-DA (conversion rate of $\text{C}=\text{C}$ bonds vs. irradiation time) containing AgNPs initiated by dye 5/Iod/amine upon exposure to a LED@405 nm in laminate. The irradiation starts at $t = 10$ s; (D) the color changes of PEG-polymers containing AgNO_3 [Color figure can be viewed at [wileyonlinelibrary.com](#)]

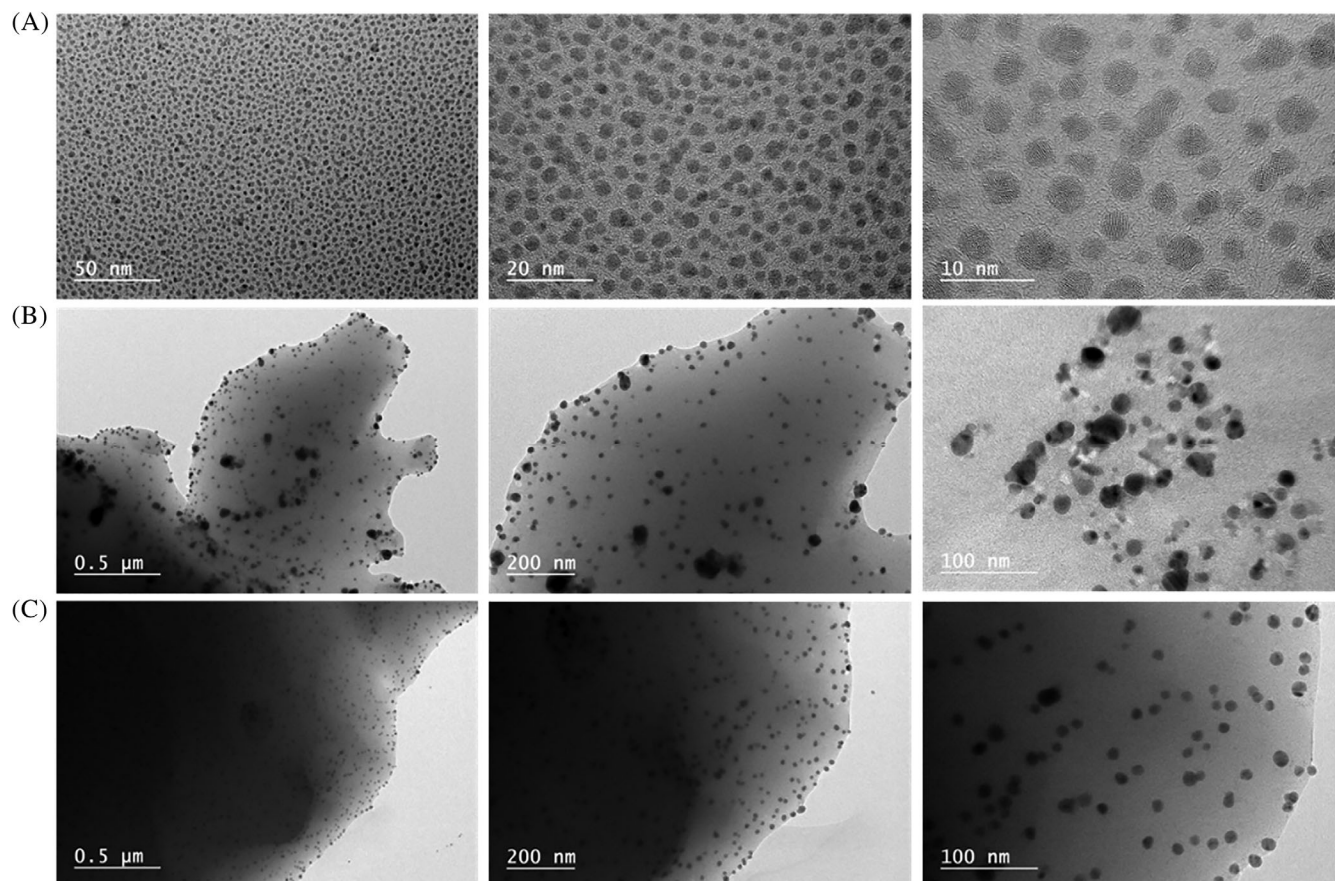


FIGURE 8 TEM images of (A) AgNPs prepared in DMF solution; (B) AgNPs prepared in PEG-polymer from FTIR experiment (thick film); (C) AgNPs prepared in thin film (PEG-based polymer)

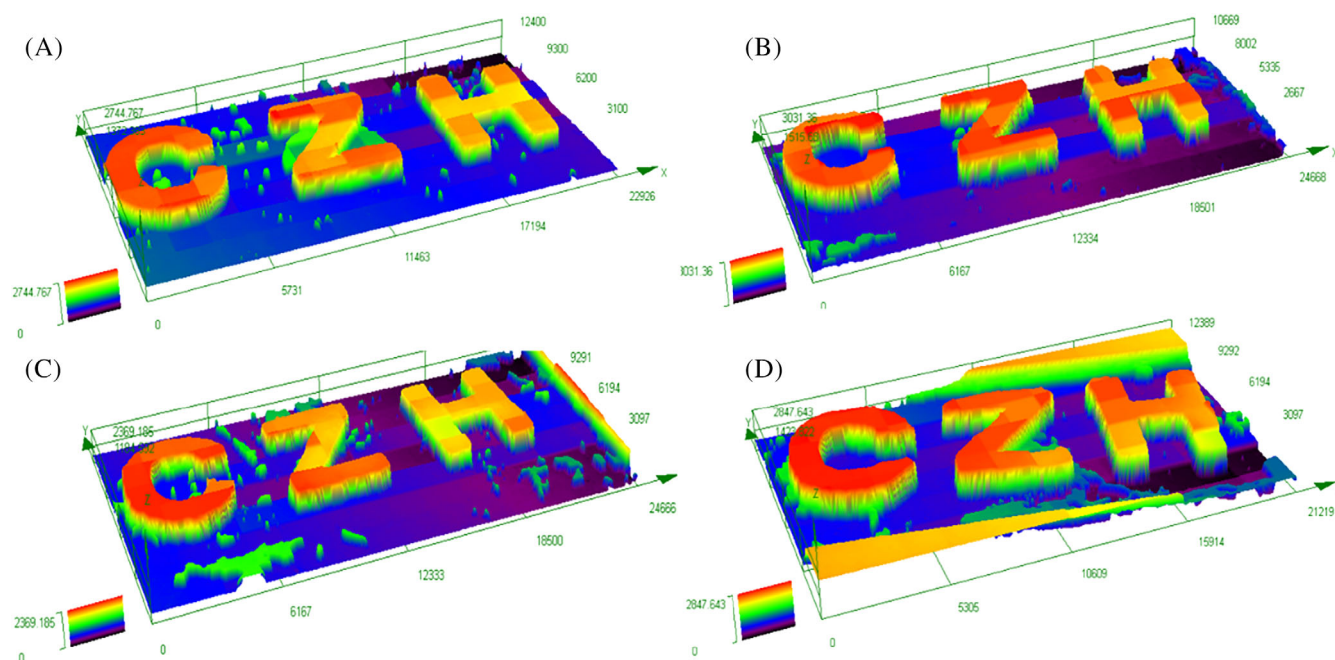


FIGURE 9 Free radical photopolymerization of PEG-DA through direct laser write experiments initiated by dyes-based PIS with a laser diode @405 nm. Characterization of the 3D patterns by numerical optical microscopy: (left) top surface morphology and (right) 3-D overall appearance: (A) containing dye 3-based PIS; (B) containing dye 5-based PIS; (C) containing dye 3-based PIS and AgNPs; (D) containing dye 5-based PIS and AgNPs [Color figure can be viewed at wileyonlinelibrary.com]

The size and the shape of the AgNPs generated in DMF and in PEG-polymers detected using TEM are depicted in Figure 8. The AgNPs in DMF were irregularly spherical with a size of about 2 ~ 4 nm, whereas the AgNPs generated in PEG-polymer were in a regular spherical shape with the size varied from 20 ~ 40 nm, which were much larger than that obtained in DMF due to the aggregation of the particles in PEG-polymer.

3.5 | The influence of AgNPs on the physical properties of PEG-polymers

3.5.1 | 3D direct laser write experiments

Since dyes 2, 3, 5, 8, and 9 were selected as excellent candidates for the FRP for PEG-DA upon irradiation with a

LED@405 nm, direct laser write experiments were carried out under these conditions. However, only dyes 3 and 5-based formulations could be successfully written and furnished stable 3D letter patterns ("CZH") with good spatial resolutions (limited by the size of the laser beam ~50 μ m). Morphologies of the 3D structures were observed using a numerical optical microscope (Figure 9). Interestingly, all direct laser write experiments could be finished within 3 min. However, a shorter irradiation time was required for the dye 5-based systems to get the 3D patterns than that used for the dye 3-based system. In addition, the color of the formulations become darker with the addition of silver cations, after laser write, the obtained polymers turned into yellowish-brown as the generation of AgNPs. Due to the photo-inhibition effect, it takes longer time to write a stable 3D pattern, whose morphology is rougher than that without AgNPs.

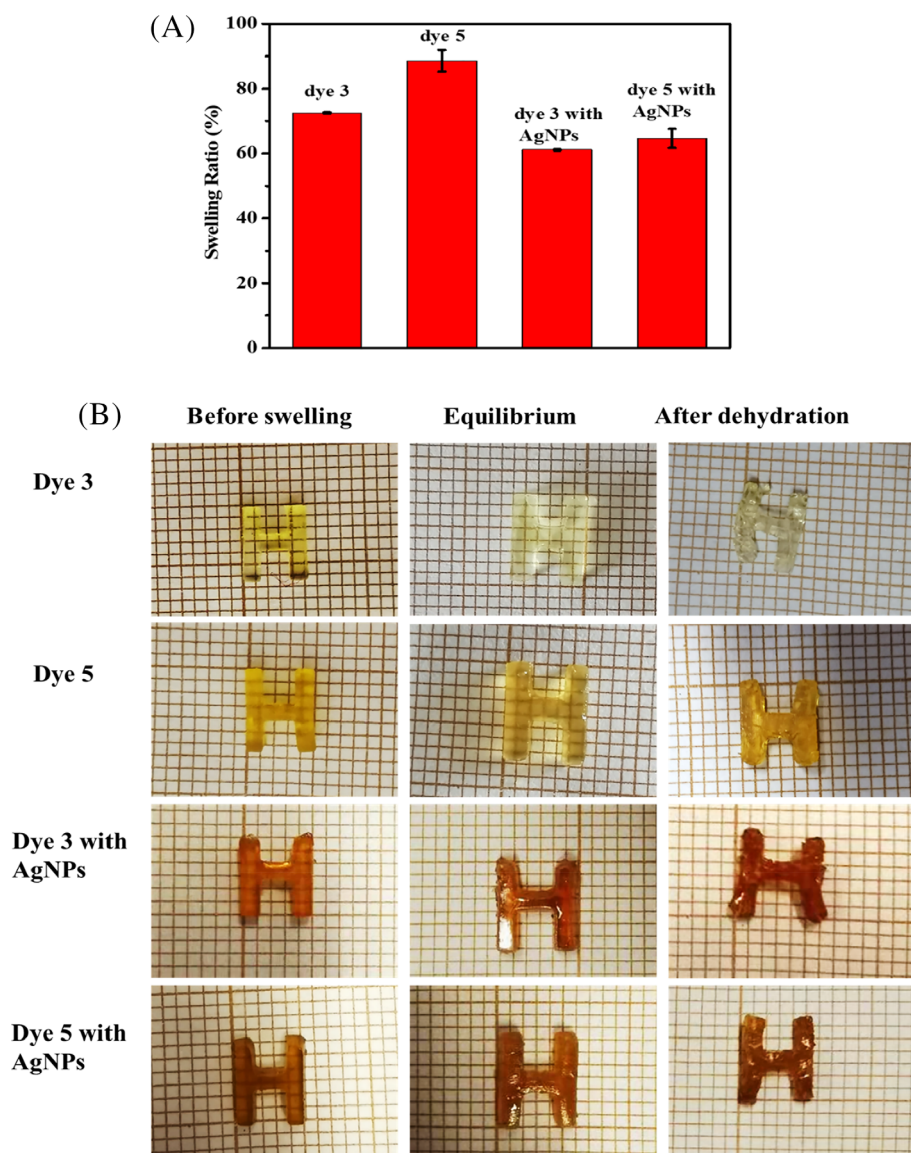


FIGURE 10 (A) The swelling ratio of PEG-polymers containing/without AgNPs; (B) the photos of PEG-polymers containing/without AgNPs during the reversible water swelling process [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 The summary of 3D pattern volumes and their increased ratio (R) during the reversible water swelling process

	Dye 3	Dye 5	Dye 3 with AgNPs	Dye 5 with AgNPs
V_1 (mm ³)	39.39	42.74	27.97	31.11
V_2 (mm ³)	69.32	81.23	40.27	49.60
V_3 (mm ³)	38.12	34.98	16.28	30.40
R (%)	176 wt%	190 wt%	144 wt%	160 wt%

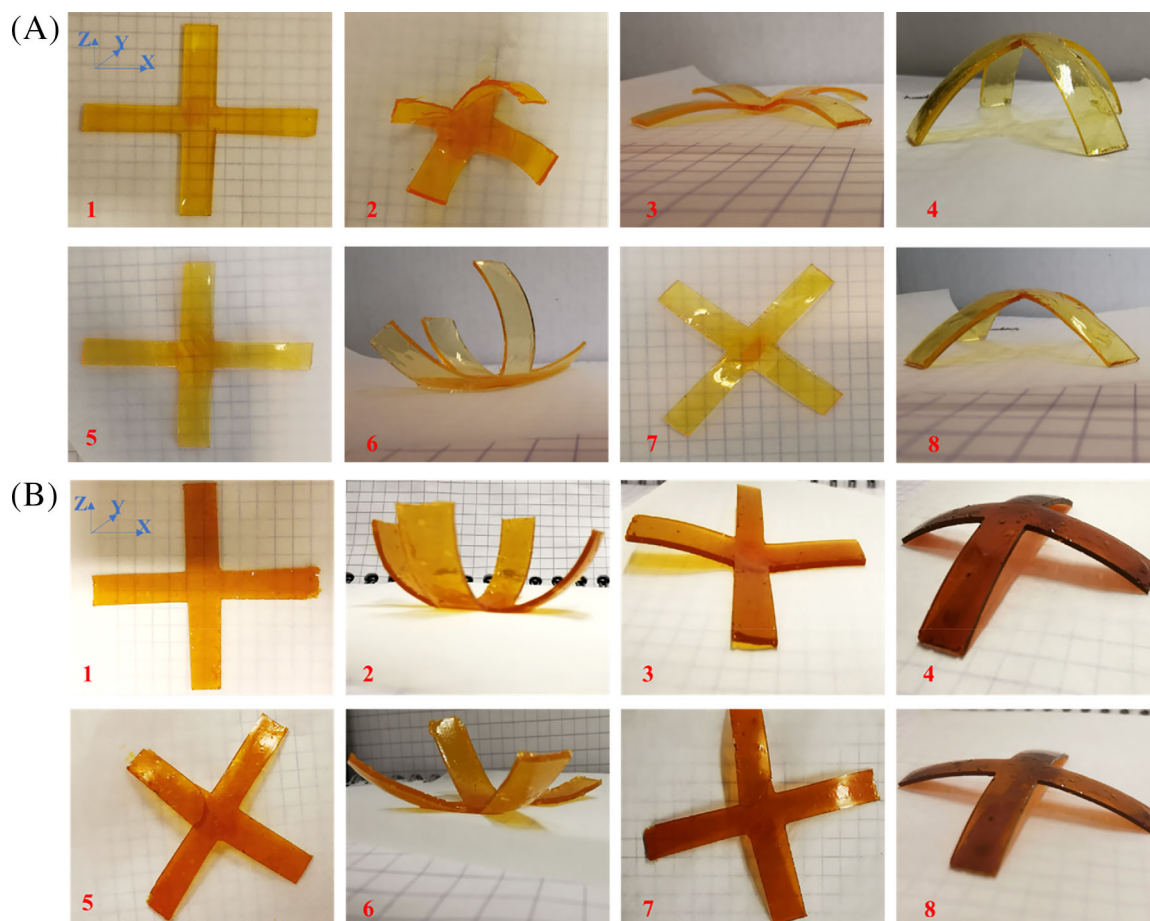


FIGURE 11 (1) Cross obtained under 1 min of light irradiation, (2) deformed cross after swelling, (3) cross restored to its original appearance after 2 min of dehydration ($T = 80^\circ\text{C}$), (4) reverse-curved cross after dehydration for 10 min, (5) cross at room temperature for 10 min; (6) deformed cross after swelling again, (7) cross recovered to its original appearance after dehydrated again for 2 min ($T = 80^\circ\text{C}$), (8) reverse-curved cross after dehydrated again for 10 min again [Color figure can be viewed at wileyonlinelibrary.com]

3.5.2 | Water swelling of PEG-polymers containing/without AgNPs

By comparing the weight and volume changes of water swelled PEG-polymers containing/without AgNPs prepared with three-component PIS based on dyes 3 or 5/Iod/amine (0.1/1.5/1.5 wt%), the effect of the presence of AgNPs for the swelling process is studied. As shown in Figure 10, after the polymers swelled in water to reach the swelling equilibrium, the swelling rate of them without AgNPs were about 70–90 wt%, and their volumes increased about 170–190 wt% (see Table 4). However, the

swelling ratio of the AgNPs-containing polymers were only about 60 wt% and the ratio of their volume increased were about 150–160 wt%, which were smaller than that achieved by the polymers without AgNPs. This may be owing to the generated AgNPs and residual salts occupied some pores inside the polymers.^{38–40} Subsequently, the polymers that reached the swelling equilibrium could return to their original weight and volume after dehydrated at 50°C for 1 h, (as shown in Figure 10(B)), while the morphologies were a little deformed, indicating that the swelling behavior of these polymers was reversible.^{41,42}

3.5.3 | The reversible shape-memory effect of PEG-polymer containing/without AgNPs

The combination of the dye 5/Iod/amine based PIS and PEG-DA can be potentially used for 3D bioprinting as its high biocompatibility and hydrophilicity. According to a previous study,⁴³ the reversible deformation effect of PEG-polymers was closely related to the irradiation time, so that the best irradiation time was selected to prepare a cross object with good spatial resolution characteristics and detect its 4D deformation upon swelling and dehydration. Subsequently, influence of the silver nanoparticles on the 4D deformation properties of PEG-polymers was also studied by comparing the shapes change performance of PEG-polymers containing/without AgNPs. As shown in Figure 11(A,B)-1, the color of the prepared cross containing AgNPs was darker than that without AgNPs. After being immersed in a water filled beaker, these two polymers all curled as swelling in water, while the degree of deformation of the polymer without AgNPs was greater than that of the polymer containing nanoparticles (the process is clearly shown in Figure 11(A,B)-2). Hereafter, the two deformed polymers were removed from the beaker and placed in an oven at 80°C to dehydrate. Interestingly, the rolled cross gradually flattened during this process and returned to its original shape after 5 min (see in Figure 11(A,B)-3). With the continue dehydrate, the restored polymers curled upside down since the contained water was completely removed, which were shown in Figure 11(A,B)-4. The above results prove that the deformation degree of the polymer containing AgNPs is smaller than that of the polymer without nanoparticles, which is consistent with their swelling performance. Finally, the reverse-curved polymers were moved from 80°C into room temperature, which gradually flatten to return their primary morphology (see Figure 11(A,B)-5). Figure 11(A,B)-6 to 8 exhibited the second shape-memory process of these two polymers, which demonstrated that the available polymers initiated by the proposed PIS can be used for 4D printing due to their reversible deformation effect through thermal-/water- responsiveness. More interestingly, the photoinhibition effect caused by the darkening of the resin with the presence of AgNPs reduces its photopolymerization efficiency, resulting in a lower crosslink density of the obtained PEG-polymer, which decrease its surface tension and surface wettability, thereby inhibiting its deformation effect.^{44–45}

4 | CONCLUSIONS

In conclusion, 12 different dyes with 2,5-diethylene-cyclopentane-1-one as the main structure were synthesized

and used as photoinitiators with Iod and EDB. Under LED irradiation, the redox reactions could take place between dyes and Iod/EDB, which generated free radicals and cations to induce the polymerization reactions of PEG-DA and EPOX monomers. Furthermore, it could also reduce the AgNO₃ into AgNPs. Owing to the extended π -conjugation in the molecular structures of the different dyes examined in this work, a strong absorption appeared in the near UV or the visible range for all chromophores, which was in agreement with their excellent polymerization efficiencies for the free radical polymerization and the cationic polymerization. Remarkably, dyes 3 and 5 proved to be excellent PIs. The steady state photolysis, fluorescence quenching, and ESR-ST experiments were successfully performed to characterize the involved photochemical mechanisms. Finally, the PEG-polymers with reversible deformation effect can also be observed and the generation of AgNPs could reduce their swelling and 4D deformation performance. In addition, the above-mentioned photocurable resins with the thermal- and water-response can be potentially used in emerging fields including biomedical engineering and smart response materials, and so forth.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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